

# Accurate Atomic Gaussian Basis Functions for Second-Row Atoms: Small Split-Valence 3-21SP and 4-22SP Basis Sets

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**ABSTRACT:** Small split-valence Gaussian 3-21SP and 4-22SP basis sets, previously reported for the first-row atoms [*Chem. Phys. Lett.*, **229**, 151 (1996)], have been extended for the second-row elements of the Periodic Table. The total energies of the ground states of the second-row atoms calculated with the new basis sets are significantly lower than those obtained with the well-known 3-21G [*J. Am. Chem. Soc.*, **104**, 2797 (1982)] and 4-31G [*J. Chem. Phys.*, **56**, 5255 (1972)] basis sets. This is because, as first noted in our previous work for first-row atoms, that the 3-21G and 4-31G basis sets only correspond to a local minimum of the Hartree–Fock energy functional, which is relatively far from its global minimum. The proposed basis sets have been tested by performing geometry optimizations and calculations of normal frequencies in the harmonic approximation of some diatomic and polyatomic molecules at the Hartree–Fock level. © 1997 by John Wiley & Sons, Inc. *J Comput Chem* **18**: 1200–1210, 1997

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## Introduction

Split-valence-type Gaussian basis sets are very effective for *ab initio* calculations of molecules, because their use significantly reduces

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the time required for calculation of two-electron integrals and their derivatives. This is because split-valence-type basis sets use the same values of primitive exponents for some of the *s* and *p* functions. Therefore, this type of basis set has become very popular in theoretical investigations of polyatomic molecules containing first- and second-row elements of the Periodic Table.

Investigations of the split-valence type of Gaussian basis sets for first-row elements of the Periodic Table, reported in a companion study,<sup>1</sup> have shown that the 3-21G<sup>2</sup> and 4-31G<sup>3</sup> basis sets

correspond to only a local minimum of the Hartree–Fock energy functional. On this basis, new 3-21SP and 4-22SP split-valence Gaussian basis sets have been introduced for H to Ne atoms, for which the Hartree–Fock total energies of their ground states are much lower than those reported earlier.<sup>2,3</sup>

The present study gives new results obtained for split-valence Gaussian basis sets for the second-row elements of the Periodic Table. We have found that the 3-21G<sup>4</sup> and 4-31G<sup>5</sup> basis sets reported earlier for these elements of the Periodic Table also do not correspond to the absolute minimum of the Hartree–Fock energy functional. This fact prompted us to construct new split-valence basis sets for the second-row elements, and these results are given in what follows. These basis sets are of the same quality as the 3-21SP and 4-22SP basis sets for the first-row elements of the Periodic Table introduced in previous work.<sup>1</sup>

The results are presented in the following order. First, an analysis of the well-known 3-21G and 4-31G basis sets for the second-row atoms is given. The new split-valence 3-21SP and 4-22SP basis sets are then described in the third section. Finally, molecular geometries and harmonic normal frequencies of some molecules obtained employing the Hartree–Fock method with the present 3-21SP and 4-22SP basis sets are compared with those calculated using existing 3-21G and 4-31G basis sets.

## Analysis of Split-Valence Basis Sets

Investigation of the split-valence type of Gaussian basis set for second-row elements has been initiated by comparing the 3-21G<sup>4</sup> and 4-31G<sup>5</sup> basis sets with their counterparts<sup>2,3</sup> for first-row elements of the Periodic Table. This comparison shows that the structures of these basis sets are very similar: the values of primitive exponents decrease irregularly for the  $1s$ ,  $2sp$ ,  $3sp$ , and  $3s'p'$  of atomic orbitals, and some of the contraction coefficients have negative values.

In our previous study<sup>1</sup> we have seen that similar characteristics of basis sets for first-row atoms are connected with the incomplete optimization of exponents and contraction coefficients. This finding led us to reoptimize the basis sets, and thus to obtain significantly lower total energies than before.<sup>2,3</sup> Therefore, we have concluded that the

3-21G<sup>4</sup> and 4-31G<sup>5</sup> basis sets for the second-row atoms must also correspond to a local minimum or saddle point of the Hartree–Fock energy functional.

This conclusion is also confirmed when one compares the values of the primitive exponents of the 3-21G and 4-31G basis sets for the sulfur atom with those of uniform quality basis sets presented in ref. 6. The values of these exponents are presented in Tables I and II, respectively. The Hartree–Fock total energies of the sulfur atom in the uncontracted and contracted 3-21G and 4-31G basis sets are shown in Tables III and IV, along with corresponding values for the other second-row atoms. The total energy of the sulfur atom in the uncontracted  $9s6p$  and  $12s8p$  uniform quality basis sets<sup>6</sup> is equal to  $-397.29344085 E_h$  and  $-397.48431537 E_h$ , respectively. In the same study, the  $9s6p$  and  $12s8p$  primitive functions have also been contracted to  $[4s3p]$  and  $[5s4p]$ . The Hartree–Fock total energy of  $^3P$  ground state of the sulfur atom in these basis sets is equal to  $-396.98859837 E_h$  and  $-397.29129697 E_h$ .

Comparison of the Hartree–Fock total energies of the sulfur atom in these basis sets shows significant advantages for the uniform quality basis sets relative to the 3-21G and 4-31G basis sets. The main improvements are achieved through the use of better exponential parameters. In the 3-21G and 4-31G basis sets, primitive exponents with values greater than 1250 and 3500 are absent, whereas in the uniform quality basis sets exponents with such large values are quite important, especially for the accurate description of the  $1s$  atomic orbital. This feature is primarily responsible for the fact that the uniform quality basis sets give total energies for

**TABLE I.**  
Primitive Exponents of the 3-21G and Uniform Quality  $9s6p$  Basis Sets of the  $^3P$  State of the S Atom.

Exp.	3-21G <sup>2</sup>	$9s6p^6$
$s_1$	1210.620000	12685.96700000
$s_2$	182.747000	1905.49340000
$s_3$	39.667300	428.40673000
$sp_4$	52.223600	115.10763000
$sp_5$	11.962900	34.48943700
$sp_6$	3.289110	10.41499300
$sp_7$	1.223840	3.22418330
$sp_8$	0.457303	0.77942289
$sp_9$	0.142269	0.21373184

**TABLE II.** Primitive Exponents of the 4-31G and Uniform Quality 12s8p Basis Sets of the <sup>3</sup>P State of the S Atom.

Exp.	4-31G <sup>3</sup>	12s8p <sup>6</sup>
s <sub>1</sub>	3442.1240000	104514.56000000
s <sub>2</sub>	518.9131000	15666.86300000
s <sub>3</sub>	116.6909000	3556.30300000
s <sub>4</sub>	31.5716500	987.26786000
sp <sub>5</sub>	127.4406000	303.72481000
sp <sub>6</sub>	29.7476700	100.62052000
sp <sub>7</sub>	8.8346640	36.08928000
sp <sub>8</sub>	2.8173900	12.97315100
sp <sub>9</sub>	3.7291850	4.83980380
sp <sub>10</sub>	1.4067700	1.86549040
sp <sub>11</sub>	0.5481100	0.49586323
sp <sub>12</sub>	0.1703809	0.15060411

the sulfur atom that are notably lower than in the 3-21G and 4-31G basis sets.

It should also be noted that, in ref. 4, mention has been made of “collapse” problems, which arise upon minimization of the Hartree–Fock energy functional with 4-31G<sup>5</sup> basis sets. Such difficulties preclude the construction of 4-31G-type basis sets for some of the atoms of the second row of the Periodic Table. Our experience shows that problems of convergence with the minimization procedure generally arise in regions that are relatively far from a point of a minimum. This is clear because near such a point any functional can be represented as a quadratic, and it is well-known that all minimization methods work well for quadratic hypersurfaces. Therefore, the “collapse” problems mentioned above clearly indicate that at

**TABLE III.** Total Energies<sup>a</sup> With Reversed Sign for the Na to Ar Atoms Obtained With the Uncontracted 9s6p and 12s8p Primitive Basis Sets.

Atom	State	9s6p		12s8p	
		Ref. 4	This work	Ref. 5	This work
Na	<sup>2</sup> S	161.00805951	161.81344457	—	161.85453864
Mg	<sup>1</sup> S	198.66809142	199.56146507	—	199.60584983
Al	<sup>2</sup> P	240.78605889	241.79874751	—	241.86575058
Si	<sup>3</sup> P	287.62880625	288.73769045	288.75624272 <sup>b</sup>	288.84126572
P	<sup>4</sup> S	339.33614961	340.54965285	340.42169083	340.70307796
S	<sup>3</sup> P	395.94904802	397.29344278	397.15746189	397.48432322
Cl	<sup>2</sup> P	457.73487147	459.23884375	459.09265517	459.45667928
Ar	<sup>1</sup> S	524.86401983	526.54076695	—	526.78739698

<sup>a</sup> Total energies in *E<sub>h</sub>*.  
<sup>b</sup> Basis set taken from ref. 9.

**TABLE IV.** Total Energies<sup>a</sup> With Reversed Sign for the Na to Ar Atoms Obtained With Contracted Basis Sets Formed From the Uncontracted 9s6p and 12s8p Primitive Basis Functions.

Atom	State	3-21G (ref. 4)	3-21P (this work)	4-31G (ref. 5)	4-22SP (this work)
Na	<sup>2</sup> S	160.85404100	161.77118100	—	161.76300940
Mg	<sup>1</sup> S	198.46810302	199.49071312	—	199.48814652
Al	<sup>2</sup> P	240.55100962	241.69672647	—	241.75545888
Si	<sup>3</sup> P	287.34439261	288.60216725	288.73293774 <sup>b</sup>	288.69592550
P	<sup>4</sup> S	339.00002698	340.38712690	340.32015611	340.51944991
S	<sup>3</sup> P	395.44743097	396.97035942	397.05120122	397.26416919
Cl	<sup>2</sup> P	457.19662002	458.89843078	458.97139798	459.19405678
Ar	<sup>1</sup> S	524.34296246	526.17747678	—	526.46999646

<sup>a</sup> Total energies in *E<sub>h</sub>*.  
<sup>b</sup> Basis set taken from ref. 9.

least the starting points in ref. 5 are very far from the absolute minimum of the Hartree–Fock energy functional. The example of the 4-31G basis set of the sulfur atom shows that a local minimum or saddle point has been taken, in ref. 5, to be the global minimum of the energy functional. Due to similarity of basis sets, as mentioned before, we can conclude that the same situation exists for the other atoms as well.

Thus, we can see that there is strong evidence that the 3-21G and 4-31G basis sets for the second-row elements of the Periodic Table do not correspond to the absolute minimum of the Hartree–Fock energy functional and hence that there is a good possibility of improving these basis sets. It should also be noted that 4-31G basis sets are only available for phosphorus, sulfur, and chlorine, and therefore their use in *ab initio* calculations of molecules is somewhat limited. Therefore, new 3-21SP and 4-22SP basis sets for all second-row elements of the Periodic Table have been constructed and are presented in the following section.

## Atomic Basis Sets

The atomic basis sets introduced in the present study have been constructed using the same program as in our previous work.<sup>1,7</sup> The ground states of the second-row atoms are used for optimization of exponential parameters and contraction coefficients. The atomic Hartree–Fock energy functional<sup>8</sup> is first minimized with respect to the exponential parameters, with the restriction that values of some *s* primitive functions are equal to those of the corresponding *p* functions, and then the process is continued for the contraction coefficients.

The total energies for the Na to Ar atoms obtained with uncontracted 9s6*p* and 12s8*p* basis sets optimized in the present study are presented in Table III and compared with those for uncontracted 3-21G<sup>4</sup> and 4-31G<sup>5</sup> basis sets. In ref. 9, the 4-31G basis set has been constructed for the silicon atom by simultaneous optimization of exponential parameters and contraction coefficients. The total energy of the silicon atom obtained with the uncontracted 4-31G basis set is also presented in Table III. Comparison of the total energies shows that those obtained in the present work are significantly lower than those for the uncontracted 3-21G

and 4-31G basis sets. For the sulfur atom the total energies are consistent with other values available in the literature. In ref. 6, the uniform quality 9s6*p* and 12s8*p* basis sets (with the restriction that *p* exponents are equal to some *s* exponents) have been optimized for the sulfur atom. The total energies are equal to  $-397.29344085$  and  $-397.48431537 E_h$ , respectively. These values are slightly higher than those obtained in the present study.

The contracted basis functions for the Na to Ar atoms optimized in this work are defined by the equations:

$$\begin{aligned}\psi_{1s}(\mathbf{r}) &= \sum_{k=1}^K d_{1s,k} \varphi_s(\alpha_{1,k}, \mathbf{r}) \\ \psi_{2s}(\mathbf{r}) &= \sum_{k=1}^L d_{2s,k} \varphi_s(\alpha_{2,k}, \mathbf{r}) \\ \psi_{2p}(\mathbf{r}) &= \sum_{k=1}^L d_{2p,k} \varphi_p(\alpha_{2,k}, \mathbf{r}) \\ \psi_{3s}(\mathbf{r}) &= \sum_{k=1}^M d_{3s,k} \varphi_s(\alpha_{3,k}, \mathbf{r}) \\ \psi_{3p}(\mathbf{r}) &= \sum_{k=1}^M d_{3p,k} \varphi_p(\alpha_{3,k}, \mathbf{r}) \\ \psi'_{3s}(\mathbf{r}) &= \sum_{k=1}^N d'_{3s,k} \varphi_s(\alpha'_{3,k}, \mathbf{r}) \\ \psi'_{3p}(\mathbf{r}) &= \sum_{k=1}^N d'_{3p,k} \varphi_p(\alpha'_{3,k}, \mathbf{r})\end{aligned}\quad (1)$$

which are similar to those used in refs. 4 and 5. The difference, however, is that a more general expression for representation of the atomic split-valence shell functions has been used in eqs. (1). The parameters *K*, *L*, *M*, and *N* define the appropriate contraction scheme of the basis functions. In the present work, three different contraction schemes have been considered. The values of the parameters are *K* = *L* = 3, *M* = 2, *N* = 1 for the (33-21); *K* = *L* = 4, *M* = *N* = 2 for the (44-22); and *K* = *L* = 4, *M* = 3, *N* = 1 for the (44-31) contraction schemes.

Comparison of the ground state wave functions of the second-row atoms obtained with uncontracted 9s6*p* basis sets shows that they fall into two groups. The first includes the wave functions for the Na to P atoms, and the second from the S to Ar atoms. The wave functions of the Al and Cl atoms are presented in Tables V and VI as exam-

**TABLE V.**  
**Solution of Hartree–Fock Equations for the  $^2P$  State of the Al Atom in the Uncontracted 9s6p Basis Set.**

$\alpha$	1s −58.48050094	2s −4.89799935	3s −0.37748866	2p −3.20556335	3p −0.18977033
0.11329401	−0.00059899	0.00969820	1.07964139	0.01687231	0.99997519
1.14261480	0.00494142	0.60192870	−0.27485053	0.38590831	−0.01449244
3.52543096	−0.00775274	0.55801254	−0.17393976	0.49477708	−0.11060972
10.83737466	0.21657411	−0.12987176	0.03636760	0.25359177	−0.04109537
33.64784884	0.52515306	−0.21907478	0.04995778	0.06406825	−0.01239948
109.64007023	0.30411356	−0.09073368	0.02089340	0.01384732	−0.00222077
400.06339907	0.08995473	−0.02449398	0.00547924		
1770.45604036	0.01828156	−0.00477975	0.00108255		
11793.72923854	0.00239448	−0.00062462	0.00013998		

ples of these two wave function types. The structure of these wave functions clearly shows that the first type can be contracted in accordance with the (33-21) contraction scheme, whereas the second is better described in the (33-12) scheme, without significant loss in total energy relative to the uncontracted values.

Corresponding analysis of the wave functions for the 12s8p basis sets shows that their structure also changes significantly from Na to Ar. There are two types of structures: the first comprises the wave functions of the Na and Mg atoms, and the second includes those from the Al to Ar atoms. For example, the wave functions of the Na and P atoms, which belong to different wave function types, are presented in Tables VII and VIII, respec-

tively. Analysis of these wave functions leads to the conclusion that the (44-31) contraction scheme is the best for the first type, whereas for the second type such a contraction scheme is inapplicable. In this wave function group, four primitives form two groups of two functions each. Therefore, only the (44-22) scheme can be used for contraction of this type of wave function.

The optimization of contraction coefficients for the 9s6p and 12s8p primitive basis functions for a given contraction scheme enables us to construct new 3-21SP and 4-22SP basis sets for the second-row elements of the Periodic Table. The total energies of these atoms obtained with the present basis sets are presented in Table IV, together with those calculated with earlier 3-21G<sup>4</sup> and 4-31G<sup>5,9</sup> basis

**TABLE VI.**  
**Solution of Hartree–Fock Equations for the  $^2P$  State of the Cl Atom in the Uncontracted 9s6p Basis Set.**

$\alpha$	1s −104.82487064	2s −10.56622977	3s −1.04090436	2p −8.02457590	3p −0.48454919
0.24627185	0.00012051	−0.02113706	0.91437591	0.01166759	0.73111277
0.86996225	−0.00038812	0.14088295	0.23741841	−0.08090698	0.39315721
3.72213855	0.00178804	0.87486581	−0.53359186	−0.52663983	−0.14947083
11.88944993	−0.07472800	0.14535267	−0.03552857	−0.44575582	−0.13500211
39.21942166	−0.49799394	−0.28016866	0.08664273	−0.13616916	−0.03792597
131.13866026	−0.41625319	−0.14313850	0.04524948	−0.02837900	−0.00791861
488.98549689	−0.13303180	−0.03999188	0.01202054		
2176.80649430	−0.02754234	−0.00778278	0.00238627		
14500.35608106	−0.00362827	−0.00102390	0.00030852		

**TABLE VII.**  
**Solution of Hartree–Fock Equations for the  $^2S$  State of the Na Atom in the Uncontracted 12s8p Basis Set.**

$\alpha$	1s −40.47738562	2s −2.79637897	3s −0.18090260	2p −1.51756062
0.04160676	0.00013389	0.00098074	−1.05312890	0.00601328
0.41713128	−0.00101897	−0.23421500	0.12104786	0.21871824
1.16235250	0.00458226	−0.64122804	0.15209871	0.42310389
3.13691110	0.00372000	−0.29672459	0.04374455	0.35912110
8.29021291	0.20777784	0.12670383	−0.01741390	0.17489148
21.95871851	0.45286664	0.18204128	−0.02865529	0.05572849
60.11032461	0.31528915	0.09175639	−0.01350080	0.01271310
176.57226717	0.12429041	0.03249319	−0.00489802	0.00308987
561.94736148	0.03590607	0.00892109	−0.00131008	
2008.73059640	0.00857560	0.00211160	−0.00031580	
8843.17387951	0.00164037	0.00040030	−0.00005898	
59005.87155763	0.00021142	0.00005169	−0.00000769	

sets. The present 3-21SP and 4-22SP basis sets themselves are given in Tables IX-A and B and X-A and B.

Comparison of the total energies given in Tables III and IV show that in all cases except for the sulfur basis set obtained in ref. 9, the present atomic total energies are lower than in previous studies. In ref. 9 the basis set has been simultaneously optimized with respect to the exponential parameters and the contraction coefficients, and the total energy of the sulfur atom in this basis set is lower than in that obtained in the present study. It is interesting to note that, for the 3-21SP basis sets, the total energies are lower because of both

better exponential parameters and contraction coefficients, whereas for the 4-22SP basis sets the improvement is caused solely by the use of better exponential parameters.

## Molecular Calculations

*Ab initio* Hartree–Fock calculations of some diatomic and polyatomic molecules have been performed for testing the new 3-21SP and 4-22SP basis sets for the second-row elements of the Periodic Table obtained in the present work. Corresponding 3-21SP and 4-31SP basis sets for the

**TABLE VIII.**  
**Solution of Hartree–Fock Equations for the  $^4S$  State of the P Atom in the Uncontracted 12s8p Basis Set.**

$\alpha$	1s −79.96514737	2s −7.50701653	3s −0.69207001	2p −5.39639697	3p −0.38942777
0.12553218	0.00031451	0.00180762	−0.64013092	−0.00357787	0.58600177
0.40064094	−0.00096470	−0.02065316	−0.58007672	0.02267956	0.51831584
1.62972925	0.00344704	−0.51076210	0.37347323	0.29512610	−0.02580441
4.30278928	−0.00532673	−0.59935721	0.22321191	0.46877552	−0.13751956
11.57634306	0.11978651	0.02661589	−0.00676806	0.30055157	−0.07208638
32.18731171	0.43892734	0.22736384	−0.06672207	0.10396021	−0.02650975
89.58495929	0.38014992	0.13040461	−0.03646688	0.02281356	−0.00521161
269.41958607	0.15786008	0.04677499	−0.01298830	0.00555118	−0.00137398
872.93283981	0.04528228	0.01257171	−0.00345507		
3140.72424901	0.01072523	0.00294269	−0.00081103		
13842.04110935	0.00204968	0.00055615	−0.00015267		
92357.70879877	0.00026420	0.00007186	−0.00001977		

TABLE IX.A.  
3-21SP Basis Sets for the Na to Ar Atoms.

Atom	$\alpha_1$	$d_{1s}$	$\alpha_2$	$d_{2s}$	$d_{2p}$
Na	248.47102766	0.86488331	6.49460139	0.16735016	0.82763041
	1099.21475690	0.17562017	20.86612762	0.57357508	0.21347098
	7320.01017255	0.02330366	68.10517280	0.35402828	0.04620771
Mg	321.28960847	0.86656933	8.58718567	0.19859933	0.82810900
	1421.53310401	0.17358024	27.01701160	0.57073610	0.21085454
	9468.12001271	0.02306231	88.08064448	0.32783062	0.04567364
Al	400.06339907	0.86776492	10.83737466	0.22119953	0.82842769
	1770.45604036	0.17213922	33.64784884	0.56662400	0.20928045
	11793.72923854	0.02289401	109.64007023	0.31053456	0.04518149
Si	473.12990622	0.86836878	12.82658551	0.22599843	0.82791361
	2094.81304780	0.17143469	39.69162349	0.56633497	0.20971725
	13955.62828382	0.02280973	129.47403982	0.30616268	0.02280973
P	513.08292993	0.86787870	13.59162817	0.19529712	0.82515660
	2274.34114677	0.17211413	42.66229825	0.57438945	0.21457368
	15151.94544206	0.02286522	139.82036038	0.32700602	0.02286522
S	429.10047704	0.86294128	10.43210743	0.06479410	0.79886860
	1909.10567091	0.17838697	34.54429948	0.56134562	0.25016598
	12715.98885260	0.02351515	115.28566038	0.45398660	0.05086938
Cl	488.98549689	0.86335580	11.88944993	0.06363089	0.79862678
	2176.80649430	0.17792925	39.21942166	0.56317356	0.25001320
	14500.35608106	0.02344138	131.13866026	0.45303954	0.05090772
Ar	558.59858877	0.86391334	13.60706499	0.06672096	0.79882484
	2487.85495144	0.17728956	44.69492563	0.56627977	0.24944607
	16573.92190582	0.02334667	149.60980979	0.44744675	0.05057537

TABLE IX.B.  
3-21SP Basis Sets for the Na to Ar Atoms.

Atom	$\alpha_3$	$d_{3s}$	$d_{3p}$	$\alpha'_3$
Na	0.60635153	0.51011058	0.48877599	0.04204431
	2.02508269	0.55189794	0.61044572	
Mg	0.85790107	0.57355367	0.48389573	0.07206199
	2.74393227	0.48410538	0.60906292	
Al	1.14261480	0.61258277	0.47588924	0.11329401
	3.52543096	0.44069202	0.61177585	
Si	1.41747555	0.61251885	0.45369543	0.16388839
	4.22201068	0.43766794	0.62814268	
P	1.55838863	0.51967461	0.38812323	0.22034376
	4.47317336	0.52884813	0.68437788	
S	0.21432503	0.87484226	0.75275946	3.22980606
	0.78345876	0.16040437	0.34297956	
Cl	0.24627185	0.81374263	0.70223876	3.72213855
	0.86996225	0.23130821	0.39700121	
Ar	0.28776986	0.78554563	0.67513936	4.30954676
	1.00805419	0.26333730	0.42617459	

**TABLE X.A.**  
**4-31SP Basis Sets for Na and Mg and 4-22SP Basis Sets for the Al to Ar Atoms.**

Atom	$\alpha_1$	$d_{1s}$	$\alpha_2$	$d_{2s}$	$d_{2p}$	$\alpha_3$	$d_{3s}$	$d_{3p}$
Na	561.94736148	0.83239318	8.29021291	0.20968897	0.77166316	0.41713128	0.18687630	0.24777554
	2008.73059640	0.19013983	21.95871851	0.47071062	0.24587058	1.16235250	0.70831804	0.48327929
	8843.17387951	0.03779888	60.11032461	0.31677325	0.05599760	3.13691110	0.15878594	0.40992238
	59005.87155763	0.00473939	176.57226717	0.12269887	0.01362284			
Mg	692.83977420	0.83367701	10.17580589	0.21783346	0.77153877	0.56453065	0.17444781	0.21798770
	2479.23513566	0.18879433	26.88307904	0.47172841	0.24610458	1.48421463	0.72669529	0.48100724
	10916.45507428	0.03764326	73.67846021	0.31134881	0.05554740	3.88805740	0.14535014	0.42846748
	72842.35243521	0.00470575	217.09037882	0.11888710	0.01331108			
Al	595.28581279	0.83227640	7.84435316	0.08860339	0.75969233	1.02702844	0.47324522	0.43521388
	2138.10104481	0.19058192	22.14917918	0.44731093	0.26515058	2.84554383	0.57185919	0.63633007
	9420.16948493	0.03784895	61.57337332	0.40729042	0.05880090			
	62847.68542369	0.00475706	184.47770208	0.17034259	0.01483406			
Si	731.10993167	0.83369708	9.68420613	0.10169375	0.76124411	1.32109381	0.50987761	0.42806093
	2628.14424648	0.18908175	27.09086423	0.45783226	0.26284309	3.56305299	0.53341058	0.63975798
	11581.04064378	0.03765241	75.34502197	0.39416686	0.05813094			
	77268.41073923	0.00471127	226.12652055	0.16102878	0.01431625			
P	872.93283981	0.83483671	11.57634306	0.11013903	0.76203850	1.62972925	0.52807824	0.41681222
	3140.72424901	0.18789116	32.18731171	0.46394981	0.26158571	4.30278928	0.51349477	0.64778594
	13842.04110935	0.03749475	89.58495929	0.38606128	0.05772956			
	92357.70879877	0.00468580	269.41958607	0.15518186	0.01395191			
S	992.96958124	0.83557729	13.06567166	0.10572295	0.76040208	1.87944449	0.49786071	0.38608298
	3576.84913332	0.18716417	36.31918553	0.46274983	0.26323355	4.87714887	0.54226236	0.67449592
	15767.60700913	0.03738270	101.24885897	0.39007346	0.05812291			
	105207.77721164	0.00466626	305.54462944	0.15631361	0.01389503			
Cl	1111.87202959	0.83618135	14.48710148	0.09890034	0.75855829	2.10703882	0.45514756	0.35157984
	4010.11959383	0.18659505	40.31473566	0.45992126	0.26517685	5.41737647	0.58368081	0.70526712
	17681.61590091	0.03728028	112.60380446	0.39651064	0.05867183			
	117980.86046310	0.00465032	341.05747400	0.15885258	0.01388550			
Ar	1233.16552904	0.83671117	15.90074003	0.09149139	0.75679618	2.31389200	0.40707137	0.31637208
	4453.13641931	0.18611062	44.31532406	0.45627568	0.26703142	5.94816287	0.63044981	0.73716507
	19639.52538669	0.03718266	124.03617925	0.40375525	0.05929867			
	131046.47324332	0.00463624	377.07378686	0.16190511	0.01388563			

**TABLE X.B.**  
**4-31SP Basis Sets for Na and Mg and 4-22SP Basis Sets for the Al to Ar Atoms.**

Atom	$\alpha'_3$	$d'_{3s}$	$d'_{3p}$
Na	0.04160676	1.00000000	1.00000000
Mg	0.07083222	1.00000000	1.00000000
Al	0.06422400	0.59864031	0.60579422
	0.19997297	0.45592907	0.48344484
Si	0.09299312	0.61371257	0.57844461
	0.29548054	0.44214995	0.51462114
P	0.12553218	0.62090850	0.55590096
	0.40064094	0.43505843	0.53813549
S	0.15195999	0.58160802	0.53338470
	0.49984510	0.47845866	0.56494619
Cl	0.18190769	0.55215437	0.50682259
	0.60311140	0.50916680	0.59206431
Ar	0.21416492	0.52488802	0.53618685
	0.70740511	0.47773574	0.61939692

first-row elements of the Periodic Table, optimized in a previous study,<sup>1</sup> have been used when required. In describing a bond between a second-row atom and hydrogen, the hydrogen basis set shown in Table XI has been used together with the 4-22SP basis set for the second-row element. The molecular *ab initio* calculations have been carried out with the aid of the HONDO-4 program.<sup>10</sup>

**TABLE XI.**  
**Contracted Basis Set for the H Atom.**

$\alpha_1$	$d_{1s}$	$\alpha'_1$
0.44453873	0.81377062	0.12194975
1.96226117	0.23472152	
13.01072961	0.03348543	



TABLE XII.  
Hartree–Fock Total Energies<sup>a</sup> (With Reversed Sign) of Various Molecules.

Molecule	3-21G	3-21SP (this work)	4-31G	4-22SP (this work)
LiCl	464.790628	466.442044	466.508015	466.738965
NaH	161.381394	162.299695	—	162.293325
HCl	457.870257	459.492813	459.545871	459.787106
AlF	339.559374	340.911579	—	341.207020
AlCl	697.958799	700.722908	—	701.056670
NaCl	618.243152	620.755732	—	621.045507
MgS	594.018024	596.447286	—	596.728338
SiS	682.980971	685.664703	—	686.012896
Na <sub>2</sub>	321.708783	323.539946	—	323.523421
Si <sub>2</sub>	574.714668	577.231984	—	577.389707
Cl <sub>2</sub>	914.543935	917.813859	917.904171	918.380980
NaOH	235.868010	236.940374	—	237.110259
MgH <sub>2</sub>	199.580635	200.585592	—	200.584529
MgCl <sub>2</sub>	1113.243345	1117.475987	—	1118.046909
AlH <sub>3</sub>	242.283138	243.395085	—	243.461820
SiH <sub>4</sub>	289.686420	290.907723	—	291.022009
PH <sub>3</sub>	340.705212	342.087454	342.022832	342.220642
H <sub>2</sub> S	396.705705	398.132237	398.204143	398.417318

<sup>a</sup> Total energies in  $E_h$ .

TABLE XIII.  
Hartree–Fock Equilibrium Geometries and Normal Frequencies<sup>a</sup> of Diatomic Molecules.

Molecule	Parameter	3-21G	3-21SP (this work)	4-31G	4-22SP (this work)	Exp. <sup>b</sup>
LiCl	$r(\text{LiCl})$	2.1122	1.9682	2.0922	1.9969	2.0207
	$\omega$	624.0	715.1	—	684.8	643.3
NaH	$r(\text{NaH})$	1.9336	1.9289	—	1.9290	1.8874
	$\omega$	1162.0	1143.7	—	1136.5	1172.2
HCl	$r(\text{HCl})$	1.2915	1.3172	1.3024	1.3232	1.2745
	$\omega$	2891.9	2834.7	2774.0	2923.3	2990.9
AlF	$r(\text{AlF})$	1.6609	1.6601	—	1.7018	1.6544
	$\omega$	—	806.5	—	753.4	802.2
AlCl	$r(\text{AlCl})$	2.2790	2.2719	—	2.3226	2.1301
	$\omega$	423.3	453.8	—	415.4	481.3
NaCl	$r(\text{NaCl})$	2.4209	2.3301	—	2.3852	2.3608
	$\omega$	346.0	395.1	—	357.2	364.6
MgS	$r(\text{MgS})$	2.2213	2.1998	—	2.2614	2.1425
	$\omega$	—	486.0	—	417.4	528.7
SiS	$r(\text{SiS})$	1.9951	2.0585	—	2.0844	1.9293
	$\omega$	719.8	758.7	—	690.8	749.6
Na <sub>2</sub>	$r(\text{NaNa})$	3.2286	3.2345	—	3.2342	3.0788
	$\omega$	155.3	156.6	—	156.2	159.1
Si <sub>2</sub>	$r(\text{SiSi})$	2.3159	2.2671	—	2.3157	2.246
	$\omega$	473.8	—	—	—	511.0
Cl <sub>2</sub>	$r(\text{ClCl})$	2.1930	2.1318	2.1929	2.1900	1.987
	$\omega$	506.8	625.5	535.3	571.5	559.7

<sup>a</sup> Bond lengths in Å, normal frequencies in  $\text{cm}^{-1}$ .

<sup>b</sup> Experimental data taken from ref. 11.

**TABLE XIV.**  
**Experimental and Hartree–Fock Equilibrium Geometries and Normal Frequencies<sup>a</sup> of Various Polyatomic Molecules.**

Molecule	Parameter	3-21G	3-21SP (this work)	4-31G	4-22SP (this work)	Exp. <sup>b</sup>
NaOH	$r(\text{NaO})$	1.8695	1.8796	—	1.9067	1.95
	$r(\text{OH})$	0.9657	0.9868	—	0.9718	0.96
	$\omega_1$ (asym. stretch)	—	3724	—	3658	—
	$\omega_2$ (band)	—	475	—	454	—
	$\omega_3$ (sym. stretch)	—	663	—	628	—
MgH <sub>2</sub>	$r(\text{MgH})$	1.7260	1.7639	—	1.7582	—
	$\omega_1$ (asym. stretch)	1667	1477	—	1474	—
	$\omega_2$ (deg. bend)	514	460	—	479	—
	$\omega_3$ (sym. stretch)	1636	1426	—	1443	—
MgCl <sub>2</sub>	$r(\text{MgCl})$	2.2478	2.2146	—	2.2631	2.18
	$\omega_1$ (asym. stretch)	612	604	—	547	—
	$\omega_2$ (deg. bend)	112	86	—	88	—
	$\omega_3$ (sym. stretch)	311	305	—	278	—
AlH <sub>3</sub>	$r(\text{AlH})$	1.5987	1.6661	—	1.6210	—
	$\omega_1$ (sym. stretch)	1982	1722	—	1825	—
	$\omega_2$ (bend)	740	673	—	691	697
	$\omega_3$ (deg. asym. stretch)	1979	1750	—	1839	1883
	$\omega_4$ (deg. asym. bend)	805	692	—	643	783
SiH <sub>4</sub>	$r(\text{SiH})$	1.4844	1.5657	—	1.5047	1.481
	$\omega_1$ (sym. stretch)	2291	2013	—	2207	2187
	$\omega_2$ (deg. deform.)	1054	884	—	941	975
	$\omega_3$ (deg. stretch)	2276	2054	—	2211	2191
	$\omega_4$ (deg. deform.)	970	834	—	872	914
PH <sub>3</sub>	$r(\text{PH})$	1.4197	1.5205	1.4330	1.4446	1.420
	$\angle(\text{HPH})$	96.11	91.92	95.10	95.88	93.3
	$\omega_1$ (sym. stretch)	2427	2152	2265	2384	2323
	$\omega_2$ (bend)	1101	1075	1107	1074	992
	$\omega_3$ (degen. stretch)	2416	2222	2277	2416	2328
	$\omega_4$ (degen. bend)	1281	1152	1266	1223	1118
H <sub>2</sub> S	$r(\text{SH})$	1.3478	1.3752	1.3543	1.3765	1.328
	$\angle(\text{HSH})$	96.02	94.30	95.57	95.35	92.2
	$\omega_1$ (sym. stretch)	2671	2575	2581	2656	2615
	$\omega_2$ (bend)	1334	1320	1328	1294	1183
	$\omega_3$ (asym. stretch)	2685	2627	2601	2704	2626

<sup>a</sup> Bond lengths in Å, bond angles in degrees, normal frequencies in cm<sup>−1</sup>.

<sup>b</sup> Available experimental data taken from refs. 12–14.

The molecular total energies obtained at the equilibrium geometries are presented in Table XII, whereas the calculated equilibrium geometric parameters of diatomic and polyatomic molecules are presented in Tables XIII and XIV, respectively. The harmonic normal frequencies of molecules calculated at these equilibrium geometries are also presented in these tables. Note that, in some cases, the normal molecular frequencies could not be determined due to convergence problems in the

iterative processes. These data are compared with those calculated with the 3-21G and 4-31G basis sets and with available experimental geometries and frequencies.

Comparison of the molecular Hartree–Fock total energies presented in Table XII shows that, in all cases, the result obtained with the new basis sets are lower than those calculated with the previous 3-21G and 4-31G basis sets. Especially large improvements have been obtained for the 3-21SP

basis sets, where, for example, the Hartree–Fock total energy of  $\text{MgCl}_2$  is lower by more than  $4.0 E_h$  relative to that calculated with the 3-21G basis set.

The equilibrium geometries and normal frequencies computed with the new basis sets are found to be at the same level of accuracy as for the existing 3-21G and 4-31G bases, although some exceptions can also be found (Tables XIII and XIV).

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